Evaluation of Performance of Sequential Membranes Used in Pilot Scale Biogas Plant: A Case Study for Laying Hen Manure

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Abstract: Poultry sector is a very important business activity in all over the Europe, especialy in Turkey and accordingly there is significant amount of waste disposal problem. One of the environmental assesment options for the use of this waste is environmentally friendly biofuel production such as biomethane. High nitrogen content is one of the important challenges to transform chicken manure to biofuel. For this reason, significant amount of dilution water is required in the systems using manure as mono substrate and thereby very large storage volumes (storage time 4-6 months) are needed for the enormous amount of effluent after anaerobic digestion process. These two subjects are threatening the economic viability of the biogas production. Furthermore, need for dilution water is an economic burden to the businesses in countries where the water scarcity is a serious concern. On the other hand, integrated use of membrane system offers possibility of using the digestion effluent as dilution water over and over where nitrogen is removed selectively by membrane assisted biogas reactor configuration. In this way, significant economy could be provided in the overall project budget by eliminating the final storage needs as well as water saving. For this purpose, the performance results of a pilot plant scale membrane system consisting of micro (MF), ultra (UF), nano (NF) and reverse osmosis (RO) membranes are presented in this study to be used in real scale applications. The feasibility of continuous reuse of digestate as fresh feed water was suggested. For this purpose, NF90 and X20 type membranes were found to be most effective ones for the recovery of ammonium (88% and 98%) from the digestate,

Keywords: Poultry waste, Laying hen manure, Ammonia removal, Ultrafiltration, Nano-filtration, Reverse osmosis.

INTRODUCTION

Chicken farming is one of the most important agricultural activities which results in huge amount of waste generation that needs environmentally friendly solution all over the world. Inappropriate management of chicken manure results in serious environmental deteriorations due to the excessive load of nitrogen in raw manure leading to eutrophication of surface waters and pollution of soil as well as ground water. The anaerobic digestion (AD) is an appropriate solution for the treatment of chicken manure but significant amount of the dilution of raw chicken manure with continuous addition of freshwater or co-digestion with other alternative organic substrates with low nitrogen content is required in order to minimize the inhibitory effect of ammonia. On the other hand, the both alternatives have their inherent disadvantages. First of all, the addition of huge level of fresh water results in construction of larger bioreactors due to increasing feed volume and the residual after fermentation needs to be stored for a long time of period until it can be used as fertilizer. This approach requires high capital cost for both main bioreactor and storage basin construction. Secondly, alternative co-substrates are also not so easily available and they are quite costly. Therefore, recycling of effluent from the fermentor after recovering of ammonia in the digestate seems to be beneficial for both reduction of the fresh water need significantly and the elimination of costly storage basin construction.

Several methods have been developed for ammonia removal including nitrification–denitrification processes [1], other biological treatments such as ANAMMOX [2-3], ion exchange processes using natural or synthetic adsorbents [4-5], membrane processes [6-9], breakpoint chlorination [10], air stripping [11], and anaerobic membrane processes [12]. Among these methods, membrane processes are powerful processes for the elimination of ammonia and other ions from wastewater due to the some advantages such as continuous operation, low foot print requirement, easy transportation, low energy requirements, low operation temperatures, and design simplicity [23]. In addition brine with high nitrogen concentration is a useful byproduct as fertilizer. Among pressure driven membrane processes, nano-filtration and reverse osmosis are the most commonly applied ones for the removal of monovalent or multivalent ions using several types of synthetic membranes.

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In order to realize the idea of using recycled effluent from digester as feed water and eliminating need for the construction of a huge storage tank, the feasibility of membrane treatment of the digestate was aimed at pilot scale. For this purpose, the performance results of a pilot plant scale membrane system consisting of micro (MF), ultra (UF), nano (NF) and reverse osmosis (RO) membranes which were previously selected using a cross-flow membrane test unit in our laboratory are presented in this study.

MATERIALS AND METHODS

Source and Characteristics of Chicken Manure

The chicken manure (laying hen) used in this study was kindly obtained from a local chicken farm in Kemalpaşa, İzmir, Turkey. The pollution characteristics of the manure are given in Table **1**. All the chicken manure was stored in a refrigerator at +4^{o}C until used.

Table 1: Characteristics of Raw Chicken Manure

Parameters	Value
pH	8.2±0.1
Conductivity (mS/cm)	7.30±0.8
SS (mg/L)	1072
COD_s (mg/L)	4610±258
NO_2^--N (mg/L)	2.8±0.5
NO_3^--N (mg/L)	108 ±7.2
NH_4^+-N (mg/L)	656±78.3
TN (mg/L)	1182±29.5
TP (mg/L)	65±2.8
Water content (%)	74±1.5
Dry matter (%)	26±1.5

SS: Suspended solids, TN: Total nitrogen, TP:Total phosphorus.

Experimental Set Up and Procedures

Experimental set-up is composed of an anaerobic digester (total volume and wet volume 100L and 70 L) and a set of membrane filtration units including MF, UF, NF and RO. Anaerobic digester as shown in Figure **1**-a was operated at 37±2 ^{o}C with help of an external heat exchanger. This reactor was fed once daily with chicken manure (2.5 L/day; 5% DM;Dry Matter) in order to provide hydraulic retention time (HRT) of 28 days corresponding to an average organic loading rate of 1.5 kg oDM/m^3/day. This bioreactor was successfully operated for 600 days with a volumetric gas production of 0.5-0.7 L/L/day having an average methane content of 58%. Throughout the operational duration, average dry matter and organic dry matter removal efficiency were observed to be 41% and 56%, respectively. The digestate from anaerobic reactor was first collected up to a reasonable volume before used for membrane filtration. Upon collection of enough amount of digestate, membrane filtration experiments were initiated. All the membrane experiments were carried out by a custom made lab-scale membrane filtration system as shown in Figure **1-b**. The system was composed of a high pressure piston pump (adjustable flow rate: 100-600 L/h; pressure up to 60 MPa) with a frequency converter, a stainless steel feed tank (60 L), permeate storage tank, retantate storage tank, membrane unit consisting of microfiltration (pore size 10 µm), ultrafiltration (UF350), nano-filtration (NF270), reverse osmosis (SW30) and a control panel (PLC) with an emergency stop button. The digestate from the main anaerobic reactor in the feed tank was filtrated sequentially using MF, UF, NF and RO membranes by the help of the piston pump after adjusting the feed pressures before each filtration mode. The feed flow rate was regulated via a valve installed before the

Figure 1: The experimental setup of **a**) pilot scale biogas system and **b**) pilot scale membrane filtration system.

module. The pressure gauges (0-100 MPa and 20 mA signal output) were installed at the inlet and the outlet of the module. The retentate flow was continuously recycled back to the feed tank after passing through the flow meter (flow range: 0-1000 L/h). The system had also a by-pass line for maintenance requirement.

Analytical Methods

The parameters such as pH, conductivity, COD, TN, NO_2-N, NO_3-N, NH_4-N, TP were measured according to the standard methods. TN was measured by Hach Lange kit. All chemical solutions were prepared with deionized water (Milli-Q® Ultrapure Water Purification System, Millipore Corp.) having conductivity less than 18.2 μS/cm. pH and conductivity values were monitored by a pH meter (WTW multi 340i) and conductivity meter (HachLange, 2100P), respectively. Volatile fatty acids (VF As) such as acetate, propionate, butyrate, isobutyrate, isovalerate, valerate, isocaprionate, caprionate and alcohols (ethanol, acetone and butanol) in the mixed liquor were analyzed using a GC (6890N Agilent) equipped with a flame ionization detector and DB-FFAP 30 m x 0,32 mm x 0,25 mm capillary column (J&W Scientific). Mixed liquor sample of 1.5 mL was first acidified with phosphoric acid and then filtered through 0.2 μm membrane before analyzed. The initial temperature of the column was 40^{o}C for 3 min followed with a ramp of 20 ^{o}C/min to 60 ^{o}C for 3 min and then increased at 30 ^{o}C/min to 120 ^{o}C for 4 min and reach a final temperature with ramp of 30 ^{o}C/min to 240 ^{o}C for 6 min. The temperatures of the injector and detector were both 240 ^{o}C. Helium was used as the carrier gas at constant pressure of 103 kPa. CH_4 content of the headspace gas was measured by injecting 5 ml bioreactor gas sample into the gas chromatograph (GC) (6890N Agilent) equipped with a thermal conductivity detector and Hayesep D 80/100 packed column. Injector, detector and column temperatures were kept at 120 ^{o}C, 140 ^{o}C, and 35 ^{o}C, respectively. Argon was used as the carrier gas at a flow rate of 20 mL/min.

RESULTS AND DISCUSSIONS

In this study, an anaerobic digester operated with laying hen manure (5% DM) and a sequential membrane filtration system at a pilot scale were operated as an integrated system. The results of the performance of sequential membrane system used were shown in Figure **2** through 4 show the results of parameters such as pH, Conductivity, SS, VFAs, PO_4-P, TCOD, OD, TN, NH_4-N, NO_2-N and NO_3-N following each membrane filtration step.

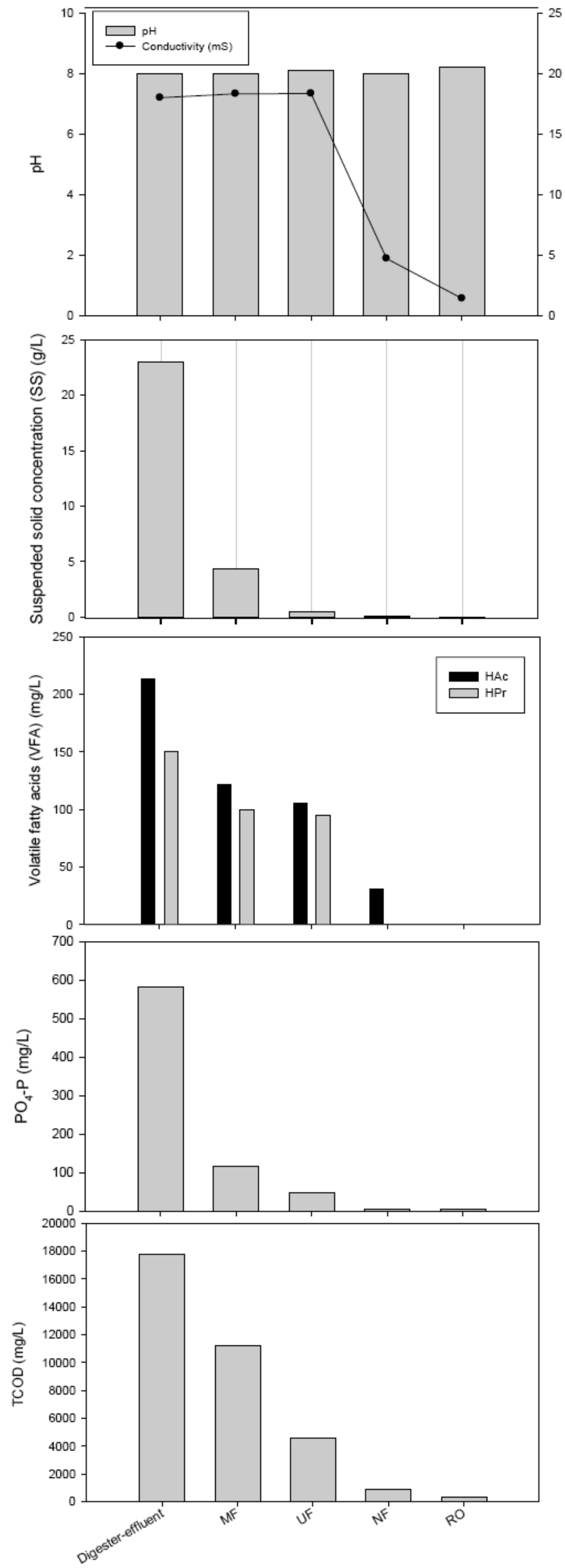

Figure 2: Characteristics of permeate from each membrane unit used in this study.

Figure **2** indicates that pH values did not change significantly and were monitored to vary between 8.0 and 8.5. The conductivity values in the effluents of bioreactor, MF and UF were observed to be similar (17-18 mS) whereas there has been a sharp decrease after NF (4.7 mS) and especially RO membrane (1.4 mS) indicating that most of the anions and cations including NH_4 are removed. In terms of SS parameter, it was seen that 82% of SS which had an initial SS of 23 g/L was retained by the MF unit and 0.1 g SS/L was achieved in the effluent of NF. No SS was detected after RO unit. Acetate (HAc) and propionate (HPr) were the main VFAs (Volatile Fatty Acids) detected in the range of 140-230 mg/L in the bioreactor effluent. Both NF and UF membrane units resulted in 50% removal of HAc and HPr on the average. Right after NF unit, the residual for HAc was 40 mg/L while there was no HPr detected. On the other hand, none of the VFAs were detected after filtration with RO unit. In terms of PO_4-P removal, the effluent concentration of PO_4-P which was 583 mg/L in the bioreactor effluent was reduced down to 118 mg/L after MF (80%). Further removal of PO_4-P was achieved via UF unit which resulted in 48 mg/L corresponding to additional 59% removal. Further filtration by NF and RO units reduced the PO_4-P concentration down to 4.1 mg/L and 3.8 mg/L, respectively. Overall PO_4-P was calculated to be around 99% and the most effective removal was initiated via MF and continued with UF and NF units. TCOD value after digestion was measured to be 18000mg/L as shown in Figure **2**. MF unit removed around 37% of the TCOD and following the MF unit, UF, NF and RO units resulted in 58%, 81% and 66% removal, respectively, which corresponded to a total COD removal of 98%.

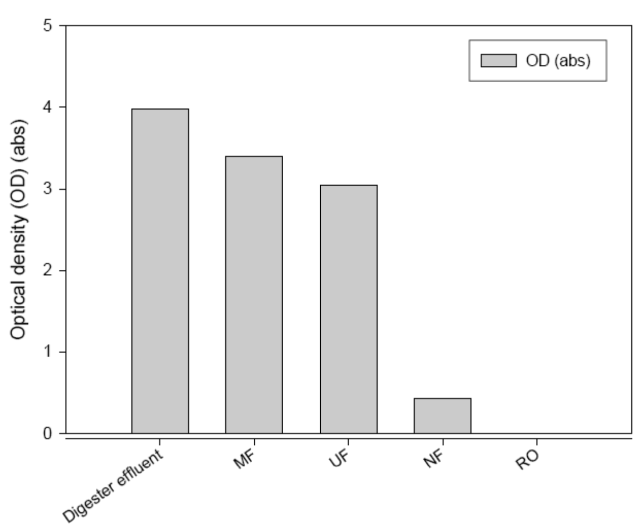

Figure 3: OD values after each membrane unit.

Figure **3** shows the optical density (OD) of permeate samples after each membrane filtration process. As shown in Figure **3**, there was not much decrease in OD values up to NF unit which was 3.97 (abs) after digestion. Right after NF unit, a sharp decrease was measured in OD value (0.42) and no OD was measured after RO unit resulting almost 100% reduction in OD value.

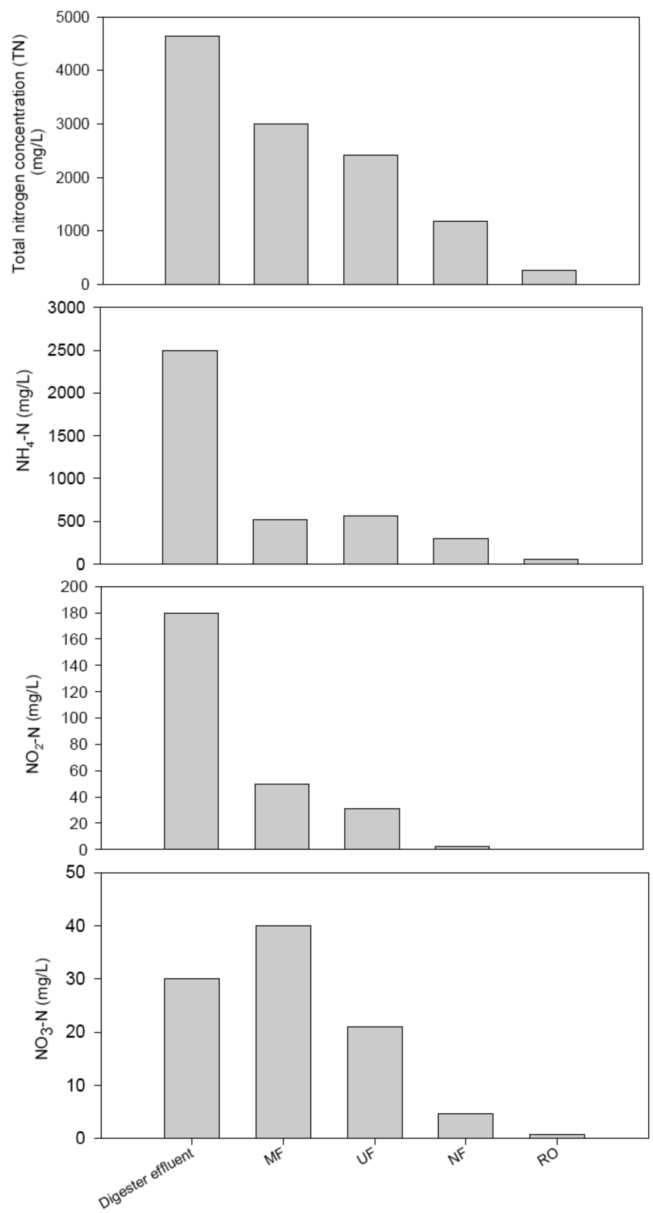

Figure 4: Nitrogen removal performances after each membrane unit.

Figure **4** shows the removal performances of each membrane unit for nitrogenous species such as total nitrogen (TN), ammonium nitrogen (NH_4-N), nitrate (NO_3-N) and nitrite (NO_2-N) after each membrane unit. The highest TN value was measured to be 4640 mg/L in the effluent of main digester. MF unit resulted in around 38% removal while UF and NF units reduced the TN concentration down to 2420 and 1180 mg/L, respectively. A sharp decrease in TN concentration was monitored right after RO unit which produced a permeate with a TN concentration of 260 mg/L. All together, an overall 94% removal of TN was achieved. NH_4-N was measured to be 2500 mg/L in the effluent of main digester which corresponds to 53% of TN. MF and UF units dropped NH_4-N down to 485 mg/L which then reached to 300 mg/L after NF unit (88% removal). Finally, the lowest NH_4-N concentration was 60 mg/L after RO unit. It was calculated that overall NH_4-N removal was 98%. In regards to NO_2-N species, it was measured to be 180 mg/L in the effluent of main digester. NO_2-N was measured to be 45 and 30 mg/L after MF and UF units, respectively. NF unit resulted in significantly low NO_2-N concentration (2 mg/L) and no NO_2-N was detected after RO unit. NO_3-N was found to be slightly higher after MF unit (40 mg/L) in comparison to the value in the digester effluent (30 mg/L). This is probably due to the partial oxidation of non-stable NO_2-N. NO_3-N was measured to be 4220 mg/L after UF unit, on the other hand, NF and RO units lowered NO_3-N concentration down to 4.6 ve 0.8 mg/L, respectively. In addition to aforementioned parameters, macro and micro element contents of permeates were measured after each membrane unit as shown in Table **2**. As shown in Table **2**, efficiency of UF, NF and RO varies depending on the element in question, on the other hand overall removal efficiency for almost all element is significantly high.

Table 2: Macro and Micro Element Contents of Permeates after Each Membrane Unit

Elements	Permeate (mg/L)		
	UF	NF	RO
B	1.6458	0.2833	0.0924
Na	303.75	44.63	3.11
Al	0.4128	0.0723	0.1245
Cr	0.0613	0.0087	0.0039
Mn	0.0453	0.0293	0.0101
Fe	2.2236	0.4710	1.4475
Co	0.0283	n.d.	n.d.
Ni	0.3446	0.0102	0.0084
Cu	0.0880	0.0512	0.1468
Zn	0.1764	0.0520	0.1474
As	0.0128	0.0015	0.0018
Se	0.0046	n.d.	n.d.
Cd	n.d.	n.d.	n.d.
Sb	n.d.	n.d.	n.d.
Ba	0.0442	0.0276	0.0409
Hg	0.0114	0.0057	0.0174
Pb	0.0140	0.0134	0.0243
Ag	0.0025	0.0069	0.0051
Sn	0.0202	0.0084	0.0338

n.d.: not detected

CONCLUSIONS

Integrated use of membrane system offers possibility of using the digestion effluent as dilution water over and over where nitrogen is removed selectively by membrane assisted biogas reactor configuration. In this way, significant economy could be provided in the overall project budget by eliminating the final storage needs as well as water saving. The feasibility of continuous reuse of digestate as fresh feed water was suggested. For this purpose, NF90 and X20 type membranes were found to be most effective for the recovery of ammonium (88% and 98%) from the digestate, which would allow the use of this concentrated retentate as a liquid fertilizer.

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AUTHOR DISCLOSURE STATEMENT

No competing financial interests exist.

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